

Correlation between molecular orbitals and doping dependence of the electrical conductivity in electron-doped Metal-Phthalocyanine compounds

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We have performed a comparative study of the electronic properties of six different electron-doped metal phthalocyanine (MPc) compounds (ZnPc, CuPc, NiPc, CoPc, FePc, and MnPc), in which the electron density is controlled by means of potassium intercalation. In spite of the complexity of these systems, we find that the nature of the underlying molecular orbitals produce observable effects in the doping dependence of the electrical conductivity of the materials. For all the MPc's in which the added electrons are expected to occupy orbitals centered on the ligands (ZnPc, CuPc, and NiPc), the doping dependence of the conductivity has an essentially identical shape. This shape is different from that observed in MPc materials in which electrons are also added to orbitals centered on the metal atom (CoPc, FePc, and MnPc). The observed relation between the macroscopic electronic properties of the MPc compounds and the properties of the molecular orbitals of the constituent molecules, clearly indicates the richness of the alkali-doped metal-phthalocyanines as a model class of compounds for the investigation of the electronic properties of molecular systems.

The electronic properties of organic molecular solids are characterized by narrow electronic bands originating from the weak, non-covalent intramolecular bonds that hold the materials together. The narrowness of the bands results in an inter-band separation that is typically much larger than the bandwidth, so that the character of each band is closely related to that of the molecular orbital from which the band originates. As the band structure plays an important role in determining the electronic properties of a material, the nature of the underlying molecular orbitals can be expected to produce observable effects in the electrical conductivity of the materials. However, it is unclear whether other phenomena (e.g., electron-electron and electron-phonon interactions or structural effects) that also play an important role in determining the electronic properties of materials can mask the effects originating from the details of the molecular orbitals.

Here we address this issue through a comparative study of the doping dependence of the electrical conductivity of six different metal phthalocyanine (MPc) compounds (ZnPc, CuPc, NiPc, CoPc, FePc, and MnPc), in which the electron density is controlled by means of potassium intercalation. We find that for all MPc's in which the added electrons transferred from the Potassium atoms are expected to occupy orbitals centered on the ligands (ZnPc, CuPc, and NiPc), the doping dependence of the conductivity has an essentially identical shape. This shape is different from that observed in MPc materials in which electrons are also added to orbitals centered on the metal atom (CoPc, FePc, and MnPc). We conclude that in MPc compounds the characteristics of the molecular orbitals of individual molecules are directly visible in the electrical conductivity of the materials.

MPc's form a large class of organic molecules [1] that are ideally suited to investigate the relation between electrical conductivity and molecular orbitals. They consist of a metal atom located at the center of a planar ligand shell formed by Carbon, Nitrogen and Hydrogen atoms

(see Fig. 1), with the metal atom determining the energy and the degeneracy of the molecular orbitals [2, 3, 4]. The different individual MPc molecules are nearly isostructural, and also their crystal structure only exhibits minor differences: this makes structural effects an unlikely origin of differences in the conductivity of different MPc compounds. Finally, MPc's have been subject of thorough investigations in the past [5, 6] and much is known about their electronic properties, which facilitate the rationalization of the experimental observations.

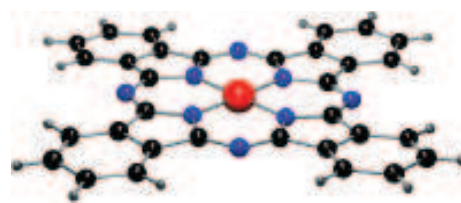


FIG. 1: Molecular structure of metal phthalocyanines: they consist of a ring of Carbon, Nitrogen and Hydrogen atoms, surrounding a metallic ion.

Doping MPc materials with electrons rather than with holes is crucial for our investigations for two main reasons. Firstly, in hole-doped MPc compounds past systematic investigations have shown that the holes always reside on the same molecular orbital centered on the ligands. This prevents the possibility to vary the molecular orbital occupied by the charge carriers responsible for electrical conductivity. On the contrary, in electron-doped MPc's the electron can either occupy a ligand or a metal orbital depending on the specific molecule considered [2]. Secondly, it is known that it is possible to transfer a larger amount of charge by reducing [7, 8] rather than by oxidizing MPc's, so that electron doping gives experimental access to a much larger interval of charge density as compared to hole doping [5, 6]. So far, however, electron-doped molecular compounds have remained vastly unexplored, probably because their sen-

sitivity to oxidizing agents increases the technical difficulties involved in their investigation.

Our work is based on thin-film (20nm thick) materials that are thermally evaporated on the surface of a silicon-on-insulator (SOI) substrate. Charge carriers are introduced in these films by means of chemical doping with Potassium atoms. All the steps of our investigations, including film deposition, doping, and electrical transport measurements, have been carried out at room temperature, *in-situ* in a single ultra-high vacuum (UHV) system with a base pressure $< 5 \cdot 10^{-11}$ mbar. This prevents the occurrence of visible degradation of the doped films over a period of days.

Figure 2A and B show the conductance of the films of six different MPc's as a function of doping concentration. The data are obtained by measuring the conductance while exposing the film to a constant flux of K atoms generated by a current-heated getter source. In order to determine the potassium concentration in the film, we have performed an elemental analysis for several doping levels using *ex-situ* RBS for CuPc. We have then used the K-CuPc data to scale the concentration of the other molecular films as a function of potassium exposure time. Although the absolute determination of the potassium concentration is affected by a relatively large uncertainty (approximately 1 K atom per molecule at high doping density), these measurements indicate that electrons transferred from the potassium atoms to the molecules are enough to fill one or more molecular orbitals, depending on the orbital degeneracy. This is consistent with past studies [2] that have shown the possibility to add at least four electrons to most of the MPc's used in our work.

We first summarize the similarities in the behavior of the conductivity of the different K-MPc compounds that have been discussed in our recent work [9]. For all the materials the conductance first increases with potassium concentration up to a high value that is comparable for the different molecules, it remains high in a broad range of concentrations, and it eventually decreases to the level observed for the pristine material. The temperature dependence of the conductance shows that all the materials are metallic in the highly conducting state and insulating in the low conductivity regions at low and very high doping. We have also shown that well-defined intercalated phases exist and that Raman studies confirm the occurrence of electron transfer from the Potassium atoms to the molecules.

We focus on the similarities and differences between the shape of the doping curve, i.e. the doping dependence of the conductivity, measured for the different MPc compounds, that have not been previously discussed. Measurements on more than 200 films demonstrate that these differences are experimentally robust. Fig. 2A shows that for CuPc, NiPc and ZnPc the behavior of the electrical conductance upon doping is very similar. In particular, the high conductivity part of the doping curve consists of two regions, which extend over the same

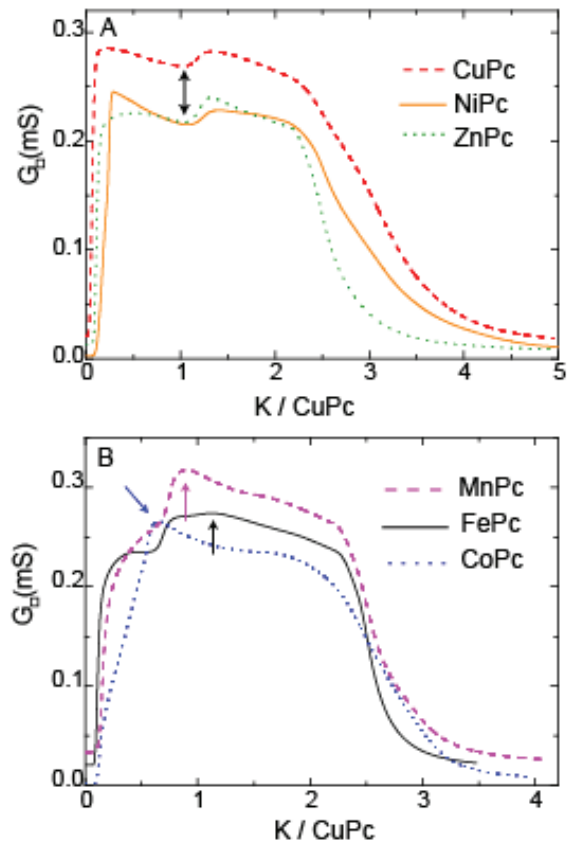


FIG. 2: Square conductance measured at room temperature as a function of potassium concentration, on 20 nm thick films deposited on Si (001) of CuPc, NiPc and ZnPc (A), and of CoPc, FePc, and MnPc (B).

concentration range. These two regions are separated by a shallow minimum, which occurs at the same doping concentration for all these three systems (indicated by the arrows in Fig. 2A). This profile of the doping curve is different from that observed for films of CoPc, FePc and MnPc (see Fig. 2B). For these systems, the doping curve exhibits only one conductance maximum, which is located at different concentrations for the three different molecules, as shown by the arrows in Fig. 2bB. In addition the precise structure of the doping curve for these three molecules is different. Specifically FePc and MnPc have a similar initial increase in the conductance upon doping, whereas the initial conductance increase is slower for CoPc. Further the conductance of MnPc continue to increase and changes the slope before reaching the maximum, whereas the increase in conductance of the FePc exhibits two steps before reaching the highest point.

The similarities and differences in the doping curves correlate well with the known way in which electrons fill the molecular orbitals of individual MPc's molecules, upon reduction. Recent theoretical calculations [2] of

the electronic structure of Metal Phthalocyanines, in agreement with spectroscopic observations [7], indicate that for all the four subsequent reduction steps of CuPc, NiPc and ZnPc the electrons fill the same, doubly degenerate $2e_g$ orbital, belonging to the ligand shell. This identical orbital filling rationalizes the identical shape of the doping curve that is observed experimentally for these three molecules upon increasing the density of charge carriers. On the contrary for CoPc and FePc, the calculations show that, respectively, the first one and two electrons fill orbitals centered on the central metal atom. Only after these orbitals have been filled, electrons are added to the $2e_g$ orbital of the ligand. This is why for CoPc and FePc films the shape of the doping curves are different from those of CuPc, NiPc, and ZnPc. It is also why the doping curves of CoPc and FePc are different among themselves, since for the first molecule only one electron is added to the $1e_g$ orbital, with strong d character [2] whereas for the second molecule, two electrons fill the $1e_g$ and a_{1g} metal orbitals. For MnPc, reliable ab-initio calculations are not available. However, based on the analysis of Ref. 2, we expect that the reduction steps with which the first three electrons are added to the molecule should involve orbitals with metal character. Thus, for MnPc, we expect a doping curve different from that of all other molecules and possibly exhibiting some similarity to that of FePc, in which two

electrons are added to orbitals centered on the metal. The comparison of the MnPc and FePc doping curves in Fig. 2B show that this is indeed the case.

In summary, we have observed that the doping dependence of electrical conductivity for six different electron-doped MPc compounds correlates with the orbitals involved in the reduction of the individual molecules. This provides a direct experimental demonstration of the role of molecular orbitals in determining the macroscopic properties of molecular materials. It is remarkable that the effect is clearly visible experimentally, in spite of the many other physical process and phenomena that determine the conductance of molecular systems in the solid state, such as for instance electron-electron and electron-phonon interaction, doping inhomogeneity, etc. The observed relation between doping-dependent conductivity and orbitals of the constituent molecules indicate that electron-doped metal phthalocyanine compounds are a unique class of materials for the systematic study of the electronic properties of molecular systems.

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